Global distribution of water isotopes retrieved from MIPAS measurements

[1]J. Steinwagner, [2]T. Röckmann, [3]N. Glatthor, [3]U. Grabowski, [3]M. Höpfner, [3]M. Milz, [3]G.Stiller, [3]T. v. Clarmann

[1]Max Planck Institute for Nuclear Physics, Heidelberg, Germany; [2]Institute for Marine and Atmospheric Research Utrecht, Netherlands; [3]Institut für Meteorologie und Klimaforschung, Karlsruhe, Germany;

Max-Planck-Institut for Nuclear Physics Heidelberg, Germany

Max-Planck-Society

Introduction

Water plays both a major role in the radiative budget [1] and in many chemical cycles on Earth. It is a nearly conserved trace species in the lower stratosphere and thus an important tracer for stratospheric transport. Because of its widely spread influence it is very important that we understand the transport of water in the atmosphere and the chemical parameters that control the sources and sinks of it in the atmosphere.

Open questions arise. Oltmans and Hofmann [2] detected that the development of stratospheric water vapor abundance shows a positive trend of 1% per year. Measurements with the satellite based instrument HALOE [3] support this observation. Furthermore the trend seems to be evident since the 1950's [4] and accumulated to an increase in stratospheric water vapor of ~2 *ppmv* (**p**arts **p**er **m**illion per **v**olume) until present This is significant because stratospheric water usually shows abundances between 3 and 6 *ppmv*. This trend cannot be explained by examinations either of the temperature trend in this atmospheric region [5] nor by the anthropogenic induced increase of methane [6] or the input of water vapor by airplane emissions. It is assumed that changes in general circulation patterns, a changing sea surface temperature, unusual El Nino phenomena or changes in Monsoon periods due to global warming contribute to this increase [7]. However, at present the sum of these effects cannot explain the entirety of the increase of water vapor.

How can isotopes assist? Isotope measurements on atmospheric trace compounds like water play an important role in the investigation of many important chemical cycles in the atmosphere. The emission of trace gases from sources, as well as removal by sink processes are usually associated with isotope fractionation, which is often very specific for the individual sources and sinks [8]. Isotopic examinations have historically been carried out using mass spectrometers due to the high sensitivity needed. Optical techniques, which form the basis of remote sensing instruments, do not yet reach the high accuracy obtained with laboratory based mass spectrometry. However, the great advantage of remote sensing systems is that the measurements can provide global coverage (*i.e.* by satellite based instruments) and are done under ambient conditions and they can distinguish between different isotopomers [*] of one species (not possible with conventional mass spectrometry). However, because of their small abundances stable isotopologues [**] and isotopomers of trace gases like water, ozone or methane are highly challenging targets for all kind of remote sensing systems.
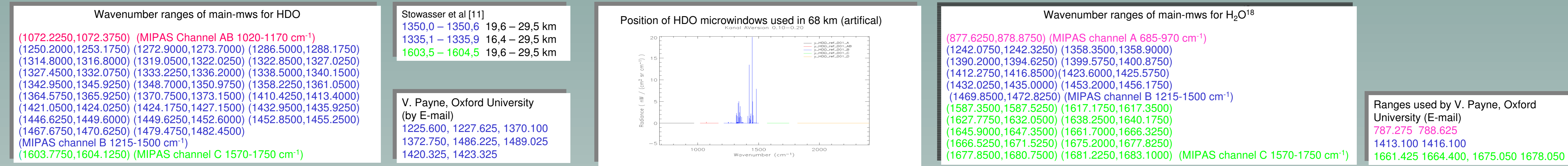
Remote Sensing of Isotopes. When examining atmospheric trace gases the infrared region is often used. The spectral region between 4 µm and 15 µm is suitable for isotope related examinations because there the isotopologues of trace gases have clear and distinguishable spectral signatures (ro-vibrational transitions). Additionally scattering is mostly negligible in this spectral region as is the influence of sunlight. This makes it possible to take measurements at day- and nighttime. Due to the weakness of the spectral signatures of isotopologues resulting from their low abundance remote sensing of stable isotopes has enormous demands both on the accuracy of the sensor systems and the mathematical methods to be used to extract profiles of atmospheric isotopic constituents from spectral measurements. Also, high spectral resolution is needed to distinguish individual lines. To retrieve altitude resolved profiles of atmospheric constituents limb sounding instruments are the preferred choice. To obtain global measurements of atmospheric parameters it is necessary to use satellite based instruments. This overview often reveals insights we cannot get from punctual measurements.

MIPAS. One of the instruments currently most suited for isotope research from space is the MIPAS (**M**ichelson **I**nterferometer for **P**assive **A**tmospheric **S**ounding) instrument. MIPAS is a Fourier transform interferometer with a spectral resolution of 0.035 cm^{-1} (unapodized) designed to study the chemistry of the middle atmosphere detecting trace gases in the mid-infrared. It is flown on Envisat on a sun-synchronous orbit (98° inclination, 90 minutes orbit period, 800 km orbit height). MIPAS is a backward-looking limb sounding instrument. A complete vertical scan from the top to the bottom of the atmosphere is made up of up to 17 spectral measurements (sweeps). The vertical step width between the sweeps is 3 km at lower heights and increases within the stratosphere. Technically, sweeps can start from 6 km and reach up to 120 km [9].

[*] isotopomers have the same number of each isotopic atom but differ in their positions, e.g. $O^{16}O^{18}O^{16}$, $O^{16}O^{16}O^{18}$, [**] isotopologue: a molecular entity that differs only in isotopic composition, e.g. CH_4, CH_3D, CH_2D_2

Spectral Database - Microwindows

Selection with KOMA (This description is taken from the abstract describing the algorithm underlying KOMA [10]) „...A novel optimization scheme has been developed for this purpose that adjusts microwindow boundaries such that the total retrieval error with respect to measurement noise, parameter uncertainties, and systematic errors is minimized. Dedicated databases that contain optimized microwindows for retrieval of vertical profiles of pressure and temperature, H_2O, O_3, HNO_3, CH_4, N_2O, and NO_2 have been generated. Furthermore, a tool for optimal selection of subsets of predefined microwindows for specific retrieval situations has been provided. This tool can be used further for estimating total retrieval errors for a selected microwindow subset...".
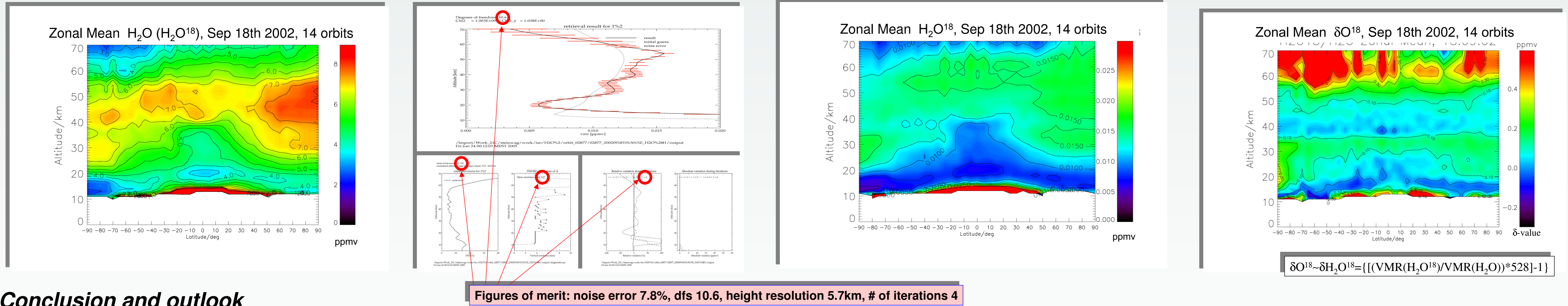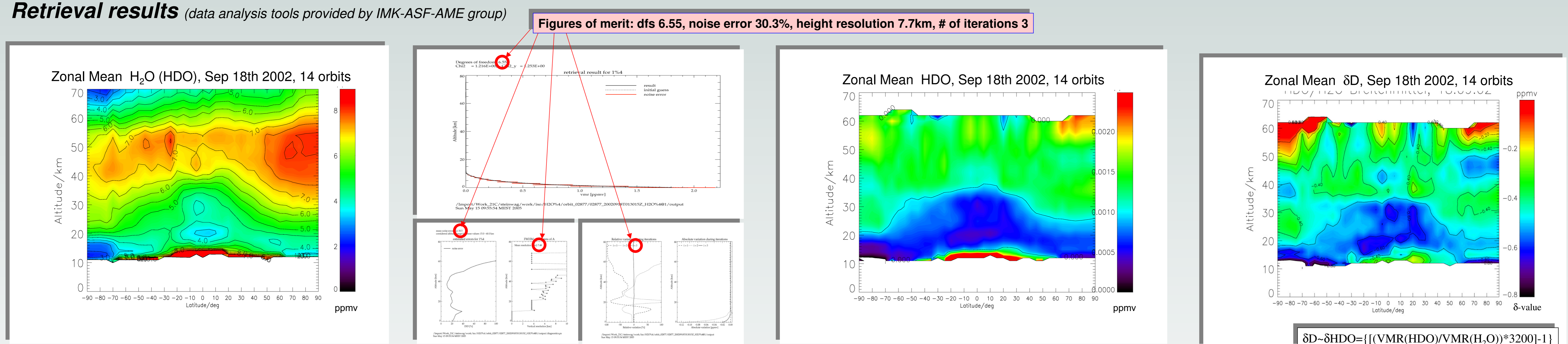

Wavenumber ranges of main-mws for HDO / Position of HDO microwindows used in 68 km (artifical) / Wavenumber ranges of main-mws for H_2O^{18}

Retrieval

Modified Least Squares approach. An optimal solution can be found by iterating [12] $x_{i+1} = x_i + (K^T S_y^{-1} K + R + \lambda I)^{-1} \cdot (K^T S_y^{-1}(y-F(x_i)) - R(x_i-x_a))$ until pre defined criteria are met or exceeded. Reliable spectral information is important but useless without proper setup of the other quantities (Regularization **R**, Jacobians **K**, *a priori* knowledge x_a, initial guess x_0 and modeled spectra F(**x**)). Also the numerical treatment is highly demanding. The retrieval is carried out using inversion software from IMK-FZK (AME group, [12]) and the radiative transport model KOPRA [13].

Expectations

δ-Notation. Isotopes are usually reported in the δ-notation. That is the deviation of a sample in isotopic enrichment from a standardized and well known quantity $\delta_I = ((R_I/R_S)-1)*1000$, where R_I= vmr[isotope]/vmr[Main isotope] R_S= Standard (i.e. SMOW), vmr (**v**olume **m**ixing **r**atio) usually in *ppmv* or *ppbv* (**p**arts **p**er **b**illion per **v**olume). It is possible to distinguish between dynamic processes (transport) and chemical processes (including photolysis) a species has undergone by examining the isotopic composition of a chemical species [8]. Such processes can either be sink or source processes for isotopes and therefore the isotopic enrichment described by the δ-notation is a valuable tool. To be able to further distinguish between sub processes of one kind We need a closer understanding of the single processes. Additionally data from satellite measurements can for instance be used as constraint for GCMs.

What can be expected from theory in the current study? Above the troposphere the vpie (**v**apor **p**ressure **i**sotope **e**ffect) gets less important compared to the oxidation of methane CH_4 through OH which creates water. This influences the isotopic composition of water. The entry d-values for HDO at the tropopause are approximately –670 per mil. We expect a gradual increase in HDO throughout the stratosphere and into the mesosphere with low values in the stratosphere. At higher altitudes we expect water to be destroyed by photolysis. This should in first approximation lead to an absolute decrease in HDO and H_2O^{18}. However, the evolution of enrichment due to photolysis depends on the wavelength of the radiance and therefore should show a somehow height dependent trend. It seems that water shows some unusual properties regarding its isotopic composition related to the oxygen anomaly isotope effect. This is to be investigated.

Retrieval results *(data analysis tools provided by IMK-ASF-AME group)*

Figures of merit: dfs 6.55, noise error 30.3%, height resolution 7.7km, # of iterations 3

Zonal Mean H_2O (HDO), Sep 18th 2002, 14 orbits

retrieval result for l²=4

Zonal Mean HDO, Sep 18th 2002, 14 orbits

Zonal Mean δD, Sep 18th 2002, 14 orbits

$\delta D \sim \delta HDO = [[(VMR(HDO)/VMR(H_2O))*3200]-1]$

Zonal Mean H_2O (H_2O^{18}), Sep 18th 2002, 14 orbits

Zonal Mean H_2O^{18}, Sep 18th 2002, 14 orbits

Zonal Mean δO^{18}, Sep 18th 2002, 14 orbits

$\delta O^{18} \sim \delta H_2O^{18} = [[(VMR(H_2O^{18})/VMR(H_2O))*528]-1]$

Figures of merit: noise error 7.8%, dfs 10.6, height resolution 5.7km, # of iterations 4

Conclusion and outlook

The theoretical predictions are met in general. Tropospheric entry values for HDO are close to the values found in literature. This indicates that water isotopes can be remotely sensed with sufficient accuracy from satellite based instruments like MIPAS. Therefore studies of time series are possible and will be the next logical step. This will give insight in seasonal variations of water isotopes and will help to improve our understanding of the processes that influence the isotopic composition of water.This in turn can aid in better identifying source and sink processes for isotopes in different atmospheric regions.

Improvements on the errors of the single profiles have to be made. Errors of the zonal mean maps have to be evaluated. Further calculations have to be made to evaluate total deuterium content and the suggested mass balance between H_2O and CH_4.

References

[1] Brindley, H. and Harries, J.E. (1998). The impact of far IR absorption on clear sky greenhouse forcing: Sensitivity studies at high spectral resolution. J. Qaunt. Spectros. Radiat. Transfer, 60(2):151-180; [2] Oltmans, S.J. and Hofmann, D.J. (1995). Increase in lower-stratosphere water vapor at a mid-latitude northern hemisphere site from 1981 to 1994. Nature, 374:146-149 ; [3] http://haloedata.larc.nasa.gov/home/index.php; [4] Rosenlof, K.H. Et al.: Stratospheric water vapor increases over the past half-century. Geophys.Res.Lett. Vol.28,No.7, 1195-1198, 2001; [6] Simmons, A. J., Untch, A., Jakob, C. (1999). Stratospheric water vapor and tropical tropopause temperatures in ecmwf analyses and multi-year simulations. Q.J.R. Meteorol. Soc., 125:353-386; [6] Röckmann, T., J.-U. Grooß, and R. Müller, The impact of anthropogenic chlorine emissions, stratospheric ozone change and chemical feedbacks on stratospheric water, Atmos. Chem. Phys., 4, 693-699, 2004, SRef-ID:1680-7324/acp/2004-4-693.[8] Ch. Bechtel and A. Zahn ,The isotope composition of water vapour: A powerful tool to study transport and chemistry of middle atmospheric water vapourAtmospheric Chemistry and Physics Discussions, 3, 3991-4036, 2003 SRef-ID: 1680-7375/acpd/2003-3-3991 [9] ESA, "ENVISAT MIPAS – An Instrument for Atmospheric Chemistry and Climate Research", ESA Special Publication SP-1229, Noordwijk (2000) ; [10] G. Echle et al, Optimized Spectral Microwindows for Data Analysis of the Michelson Interferometer for Passive Atmospheric Sounding on the Environmental Satellite Applied Optics, Volume 39, Issue 30, 5531-5540, 10/2000;[11] Stowasser, M., H. Oelhaf, G. Wetzel, F. Friedl-Vallon, G. Maucher, N. Seefeldner, O. Trieschmann, T. Von Clarmann, and H. Fischer, Simultaneous measurements of HDO, H₂O, and CH₄ with MIPAS-B: Hydrogen budget and indication of dehydration inside the polar vortex, J. Geophys. Res., 104, 19213-19225, 1999. [12] T. von Clarmann, N. Glatthor, U. Grabowski, M. Höpfner, S. Kellmann, M. Kiefer, A. Linden, G. Mengistu Tsidu, M. Milz, T. Steck, G. P. Stiller, D. Y. Wang, H. Fischer, B. Funke, S. Gil-López, and M. López-Puertas, Retrieval of temperature and tangent altitude pointing from limb emission spectra recorded from space by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS), J. Geophys. Res., Vol. 108, No. D23, 4736, doi:10.1029/2003JD003602, 2003. [13] Stiller, G. P., "The Karlsruhe Optimized and Precise Radiative Transfer Algorithm (KOPRA)"; Forschungszentrum Karlsruhe, Wissenschaftliche Berichte, FZKA 6487 (2000)